

**CHARACTERIZATION OF SURFACE FUNCTIONALITY OF COALS BY
PHOTOACOUSTIC FTIR (PAIFT) SPECTROSCOPY, REFLECTANCE INFRARED
MICROSPECTROMETRY, AND X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)**

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This paper illustrates detection by the technique of PhotoAcoustic Infrared Fourier Transform (PAIFT) spectroscopy of new carbonyl-type functionality at the surfaces of powdered bituminous coals, generated by both base-promoted and by thermal decomposition of precursor peroxide species, postulated as ubiquitous constituents at the surfaces of all except the most freshly prepared samples. In artificially oxidized coals, there are quantitative associations between the level of carbonyl content revealed by PAIFT spectra and plastic properties of the coals. In additional, related studies, we have derivatized and quantified the hydroxyl group content of the oxidized coals by trifluoroacetylation, followed by hydrolysis and anion-chromatographic analyses for trifluoroacetate. PAIFT and Fluorine-XPS spectra of the trifluoroacetylated species are discussed. Maceral components and mineral inclusions have been identified and characterized in sectioned, polished surfaces of Canadian bituminous coals using reflection FTIR microspectrometry; this direct examination shows promise for real-time monitoring of various reactions at surfaces.

INTRODUCTION

Sensitivity enhancements in spectroscopy show promise of specific characterization of functional groups in coals and their chemical transformations. We have applied one of the newer techniques (PhotoAcoustic Infrared Fourier Transform spectroscopy (PAIFT spectroscopy)) to generate a data base of coal samples amounting to several thousand spectra. Various preliminary reports of our results have been published or presented (1-7).

Among the manifold advantages possessed by PAIFT spectroscopy for the study of coals are minimal sample preparation, insensitivity of signal to degree of subdivision, and the ability to observe surface features generated by chemical transformations. PAIFT spectra of coals do not exhibit the sloping baselines characteristic of alkali halide pellet spectra (contrast a recent report of such FTIR spectra of Canadian coals (8)), and subtraction to yield difference spectra revealing introduced features is straightforward and avoids arbitrary scaling procedures. The first paper of this series (7) reported detection by PAIFT spectroscopy of new carbonyl oxygen functions at the surfaces of powdered bituminous coals, derived from base-promoted or thermal decompositions of precursor peroxide species, which we suggested were present ubiquitously as surface entities for all except the most freshly prepared samples. In more recent work, we have discovered that thermal decompositions accompany a standard vacuum drying procedure.

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EXPERIMENTAL

PhotoAcoustic Infrared Fourier Transform (PAIFT) Spectra

Spectra were obtained using a Bruker IFS110 purge-type Infrared Fourier System with a Ge on KBr beamsplitter. The interferometer compartment of the spectrometer was acoustically insulated from the sample compartment using a box fabricated from expanded polystyrene. The modulated source radiation was reflected into a E G & G Princeton Applied Research Model 6003 Photoacoustic accessory fitted with a zinc selenide window and the amplified photoacoustic output was transmitted to the data system of the IFS110. The nitrogen purge flow was interrupted during scanning.

In the standard operating mode, 10-50 mg of the dried coal were placed in the sample cup, and 128 photoacoustic interferograms were collected at 8 cm^{-1} resolution with a zero-filling factor of 2, corresponding to a final transformed spectrum encoded every 4 cm^{-1} . The photoacoustic spectra were obtained by ratioing against the energy output (black-body response) from a similarly dried sample of Fisher Carbon Lampblack C-198. The interferometer mirror velocity was 0.08333 cm s^{-1} , and spectra were acquired from 4000 to 400 cm^{-1} . The difference spectra illustrated in Figures 1 through 6 were obtained by least-squares subtraction over the range 2000 - 1400 cm^{-1} .

Preparation of Coal Samples for Spectroscopy

The coals were ground to the range 50-60 mesh under liquid nitrogen using a Brinkmann Pulverizer, and were dried at 100°C under vacuum for 6 h before transfer to the sample cup of the photoacoustic accessory.

High-Pressure Oxidations of Coal Samples

The coals were ground and sized to 50 mesh and were subjected to oxidation by air at 55°C and 9 MPa for periods ranging from 3 to 196 h. All samples were subjected to the standard drying procedure before PAIFT spectroscopic examination.

Analytical and fluidity data on the as-received coal samples are presented in Table 1.

FTIR Microspectrometry

Spectra were acquired (250-500 scans) using a Spectra-Tech IR-PLAN accessory and a Nicolet 20SX spectrometer, at a resolution of 4 cm^{-1} ; spectra are referenced against an equivalent area of a gold-surfaced mirror.

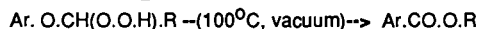
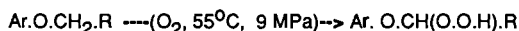
DISCUSSION AND RESULTS

(a) Generation of Carbonyl Functionalities from Thermal Decompositions of Peroxides at Surfaces of Coals Subjected to "Accelerated Oxidations" at High Pressure

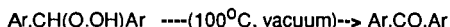
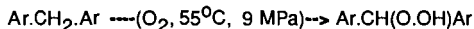
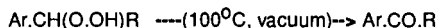
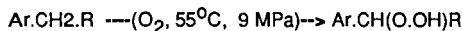
The recorded sensitivity of FTIR spectroscopy in detecting oxidative change in coals is significantly less than that of standard plasticity tests; thus, Painter and his colleagues (9), employing standard KBr pellet "transmission" FTIR spectroscopy, found less than a 1 % increase in the ratioed intensity of carbonyl bands for coals oxidized at 60°C or 140°C for periods sufficient to decrease Gieseler fluidity by over 90 %.

We have compressed the time scale of oxidative changes by subjecting powdered coals to pressurized air at slightly elevated temperatures. With such samples, we observe distinct, readily differentiated types of carbonyl absorptions (around 1750 , 1720 , 1690 , and 1650 cm^{-1}) whose relative proportions are *different* for different coals, and we propose that the carbonyl species are generated by the standard vacuum drying procedure from thermal decomposition of the assumed peroxide species. Representative difference spectra taken for the six coals of Table 1 at the stage of 48 hours oxidation are reproduced in Figures 1 through 6.

We suggest that these peaks arise from different, specific decompositions of peroxides occupying different structural sites in the coals. The 1750 cm^{-1} and 1720 cm^{-1} peaks are attributed to decompositions of α -hydroperoxyethers to yield cyclic or open-chain esters; the 1750 cm^{-1} (lactone species) from a cyclic ether precursor, and the 1720 cm^{-1} from an open-chain precursor, that is:



Stock and Wang (10) have recently postulated generation of lactone species from the ruthenium (VIII)-catalyzed oxidation of Illinois No. 6 bituminous coal by sodium periodate. The 1690 and 1650 cm^{-1} peaks are attributed to decompositions of α -hydroperoxy aralkanes or of hydroperoxy diarylalkanes, that is:



(b) *Associations of Carbonyl Absorption Intensities with Other Coal Properties*

The relative intensities of the four carbonyl absorptions for the six coals examined are dependent in a complex manner upon oxygen content, carbon/hydrogen ratio, and the progress of oxidation, but there are general *quantitative* associations of increasing carbonyl intensities with many characteristics of the behavior of the sequences of oxidized samples for a given coal. These include relationships between carbonyl intensity and oxygen content for the Greenhills coal (Western Canadian: bituminous high-volatile 'A'), carbonyl intensity and Gieseler fluidity for the Greenhills and Fording (Western Canadian: bituminous high-volatile 'A') coals, and for the Barton and McClure coals (U.S.A., bituminous high-volatile 'A' and medium-high volatile 'A'), illustrated in Figures 7 through 13. However, the coals are behaving in sufficiently different fashions (both in the quantitative distribution of the various introduced carbonyl species, in their qualitative rates of generation, and in the nature of the influence of changed functionality on the technical properties) that generalized treatment as a single data set would obscure the individual correlations. In view of our findings, we suggest that caution would be appropriate in using the approaches adopted by Fredericks and his co-workers (11), where attempts are made to make generalized predictions of technological properties using principal factor analyses of FTIR spectra of a wide range of coals.

(d) *Trifluoroacetylation as a Derivatization Technique for Hydroxyl Content of Coals*

Acetylation via acetic anhydride/pyridine is a standard derivatization method for analysis of hydroxyl content of coals, but the quantitative nature and the selectivity of these reactions are not established; there are significant difficulties in using FTIR difference spectroscopy and the acetate carbonyl intensity to define the nature of hydroxyl groups (that is, phenolic or alcoholic?). Since these differences arise in part from peak overlap of acetate carbonyl with the 1600 cm^{-1} absorption of coals, we have employed trifluoroacetylation (where the trifluoroacetate carbonyl absorbs around 1800 cm^{-1}) as an alternate technique. The trifluoroacetate ion may be analyzed readily by anion chromatography after hydrolysis of the trifluoroacetylated coal, and quantitation of the trifluoroacetyl group is also possible by calibration against the intensity of the fluorine and trifluoromethyl-carbon signals in the X-ray photoelectron spectra of such samples.

(e) *Reflection FTIR Microspectrometry of Coals*

We have conducted preliminary examinations of sectioned, polished surfaces of samples of Eastern and Western Canadian bituminous coals using the IR-PLAN accessory in the reflectance mode, referenced against a gold mirror. Representative spectra are reproduced as Figures 14 through 17. The significant differences among the microscopically distinguishable components, and the ease of detection and identification of mineral inclusions, suggest that direct examinations of coals undergoing chemical transformations (such as the base-promoted and thermal transformations discussed in this paper and our earlier work) could be profitably examined using this accessory FTIR device.

CONCLUSIONS

We have indicated the potential for surface characterization of several techniques under study in our laboratory. We suggest that the evidence for previously unquantified and undetected peroxide species on coal surfaces presented above and in an earlier Symposium (7) requires reconsideration of the influence of the proportion of surface peroxides upon the course(s) of coal pyrolyses, and provides strong support to recent proposals (12) recommending storage of laboratory samples of coals in sealed ampoules.

ACKNOWLEDGEMENTS

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Table 1
Coal Samples Subjected to High-Pressure Oxidations
Analytical and Fluidity Data on Fresh Coals

Coal Designation	Classification	C, %	H, %	O, %	Gieseler Fluidity (dd/min)
Greenhills (Western Canadian)	HV 'A'	81.56	4.75	4.79	24
Fording (Western Canadian)	HV 'A'	80.49	5.07	5.60	365
Barton (U. S. A.)	HV 'A'	81.81	5.08	4.34	20350
McClure (U. S. A.)	MV-HV 'A'	83.07	4.74	3.82	7900
Alto (Appalachian, U. S. A.)	HV 'A'	79.69	5.20	7.47	1580
Basset	L-MV	85.01	4.42	3.20	32

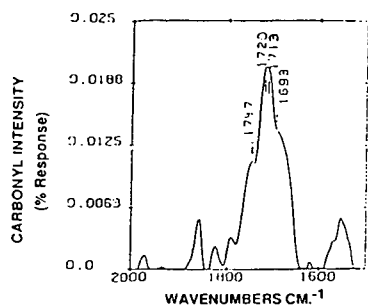


Figure 1
PAIFT Difference Spectrum
Greenhills Coal: (Oxidized 48 h) - (Fresh Coal)

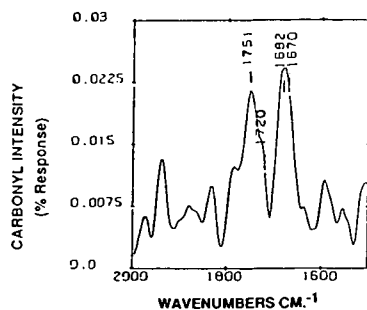


Figure 2
PAIFT Difference Spectrum
Fording Coal: (Oxidized 48 h) - (Fresh Coal)

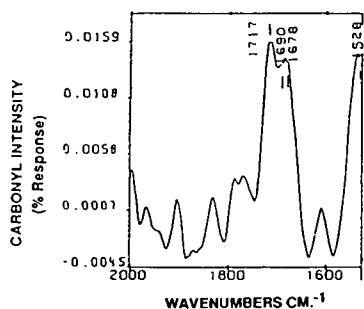


Figure 3
PAIFT Difference Spectrum
Barton Coal: (Oxidized 48 h) - (Fresh Coal)

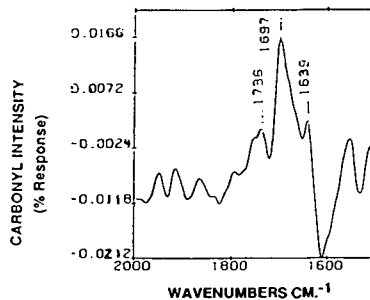


Figure 4
PAIFT Difference Spectrum
Alto Coal: (Oxidized 48 h) - (Fresh Coal)

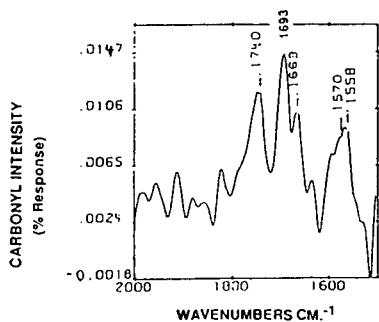


Figure 5
PAIFT Difference Spectrum
McClure Coal: (Oxidized 48 h) - (Fresh Coal)

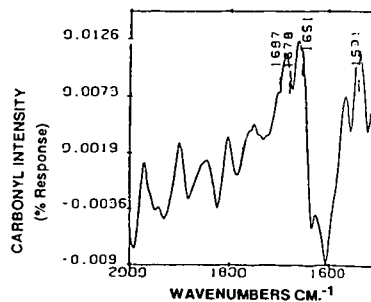


Figure 6
PAIFT Difference Spectrum
Basset Coal: (Oxidized 48 h) - (Fresh Coal)

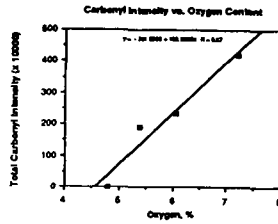


Figure 7
Greenhills Coal - Carbonyl Intensity (PAIFT Spectra) vs. Oxygen %

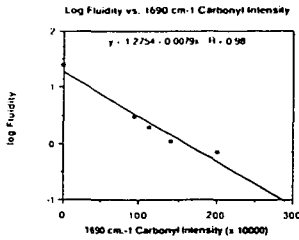


Figure 8
Greenhills Coal - log Fluidity vs. 1690 cm⁻¹ Carbonyl Intensity (PAIFT Spectra)

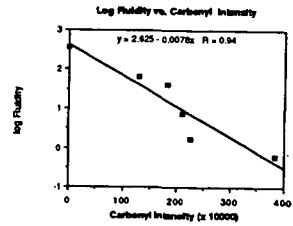


Figure 9
Fording Coal - log Fluidity vs. Carbonyl Intensity (PAIFT Spectra)

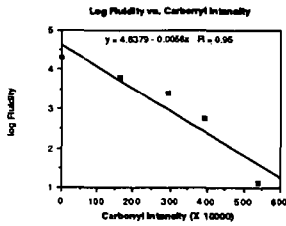


Figure 10
Barton Coal - log Fluidity vs. Carbonyl Intensity (PAIFT Spectra)

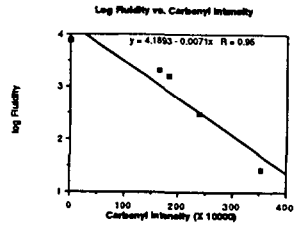


Figure 11
McClure Coal - log Fluidity vs. Carbonyl Intensity (PAIFT Spectra)

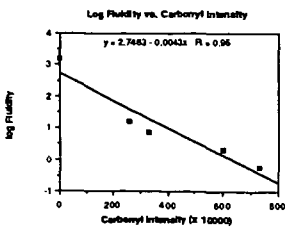


Figure 12
Alto Coal - log Fluidity vs. Carbonyl Intensity (PAIFT Spectra)

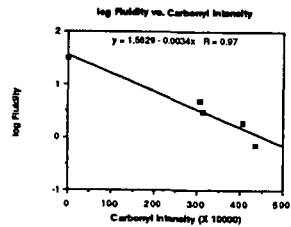


Figure 13
Besset Coal - log Fluidity vs. Carbonyl Intensity (PAIFT Spectra)

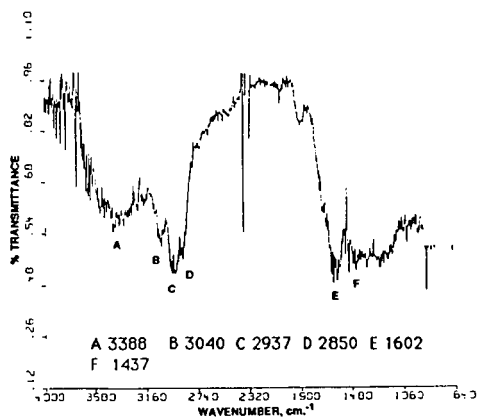


Figure 14

Western Canadian Bituminous Coal
FTIR Microspectrum of Vitrinite Component

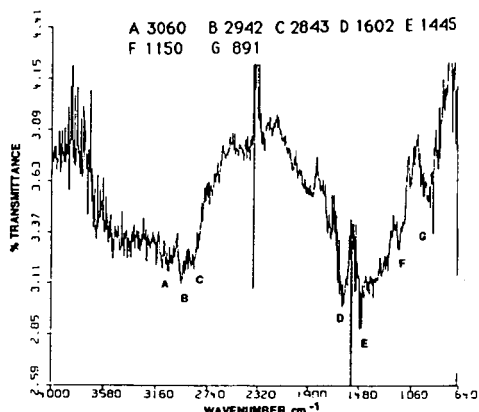


Figure 15

Western Canadian Bituminous Coal
FTIR Microspectrum of Fusinite Component

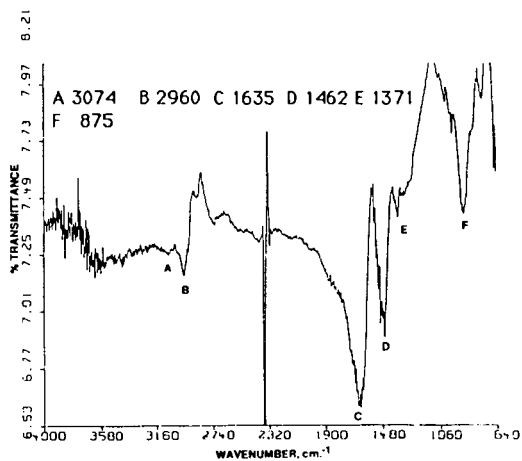


Figure 16

Cape Breton Island Bituminous Coal
FTIR Microspectrum of Vitrinite Component

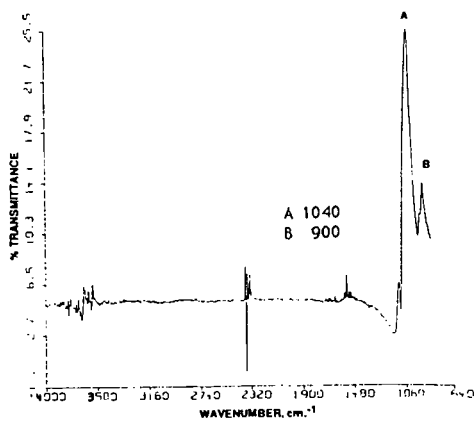


Figure 17

Cape Breton Island Bituminous Coal
FTIR Microspectrum of Kaolinite Inclusion